

Donor–Acceptor Compounds. IX*. Pyridine, 2-, 3- and 4-Methylpyridine N-oxides Complexes with SbCl_3 and SbCl_5 .

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The interaction of SbCl_3 and SbCl_5 with pyridine, 2-, 3- and 4-picoline N-oxides by spectrophotometric, dielectrometric and conductometric titrations has been investigated. The formation of complexes in 1:1 and 1:2 molar ratio for SbCl_3 and adducts 1:1, when the acceptor was SbCl_5 , is confirmed. The dipole moments of the formed complexes have been calculated. The following adducts: $\text{SbCl}_3 \cdot \text{PyO}$, $\text{SbCl}_3 \cdot (4\text{-PicO})_2$, $\text{SbCl}_5 \cdot \text{PyO}$, $\text{SbCl}_5 \cdot 2\text{-PicO}$, $\text{SbCl}_5 \cdot 3\text{-PicO}$, and $\text{SbCl}_5 \cdot 4\text{-PicO}$ have been isolated and their most significant IR frequencies are reported and assigned. Those located within $600\text{--}250\text{ cm}^{-1}$ range are consistent with a C_{4v} symmetry for SbCl_5 complexes. All the isolated solids are non-electrolytes in acetonitrile.

Introduction

The coordination chemistry of the pyridine N-oxide and its derivatives has been the subject of recent revisions^{1,2}. As far as the behaviour of these bases with acceptors which contain non-transitional elements is concerned, the interaction with halides and haloderivatives of Te, P, Si, Ge, Sn, Pb, B², Al³ and In⁴ has been studied. The preparation of the adduct $\text{SbCl}_5 \cdot \text{PyO}$ has been also described⁵. On the other hand, there has recently been reported the isolation and properties of the adducts formed by the bases previously mentioned and Sb(OR)Cl_4 ⁶.

The results obtained from the study of complex formation between SbCl_3 or SbCl_5 and pyridine N-oxide (PyO , $\text{C}_5\text{H}_5\text{NO}$) and picoline N-oxides (2-PicO, 3-PicO, 4-PicO; $\text{C}_6\text{H}_7\text{NO}$) are now reported.

Experimental

Materials

Acetonitrile, 1,2-dichloroethane and dichloromethane were purified by usual methods. Benzene Carlo Erba

for Spectrophotometry was dried over Molecular Sieves 4 A. Antimony pentachloride Carlo Erba was vacuum distilled. Antimony trichloride Merck was purified by sublimation under vacuum. Pyridine N-oxides Fluka were recrystallized from acetone and benzene.

Preparation of Complexes

The adducts $\text{SbCl}_3 \cdot \text{L}_n$ ($n = 1$ or 2) were prepared in benzene or in 1,2-dichloroethane by mixing solutions which contained the acceptor and the donor in a proportion slightly higher than the 1:2 acceptor/donor molar ratio (MR). When $\text{L} = \text{PyO}$, the compound was isolated in benzene, washed with acetone and then vacuum dried. When $\text{L} = 2\text{-PicO}$ and 3-PicO , using 1,2-dichloroethane, solids which contained a mixture of the adducts 1:1 and 1:2 were obtained. For $\text{L} = 4\text{-PicO}$ the complex was prepared in 1,2-dichloroethane, washed with the same solvent and vacuum dried.

The adducts $\text{SbCl}_5 \cdot \text{L}$ were isolated in 1,2-dichloroethane, except $\text{SbCl}_5 \cdot 3\text{-PicO}$ which was prepared in a mixture of the above mentioned solvent and cyclohexane. The donor and the acceptor were then mixed in an approximately 1:1 molar ratio. When $\text{L} = \text{PyO}$ or 4-PicO , the reaction proved to be strongly exothermic and produced the immediate formation of a precipitate which was washed several times with hot 1,2-dichloroethane. When $\text{L} = 2\text{-PicO}$ and 3-PicO , it was necessary to eliminate most of the solvent and to cool the solution to induce the precipitation.

Analytical Procedure

Sb(III) was determined volumetrically⁷. C, N and H were analyzed with a Perkin Elmer 240 apparatus in the Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Zaragoza (Spain). The analytical results, together with the colour and the melting points of the adducts are given in Table I.

Physical Measurements

Conductometric and spectrophotometric studies were carried out employing the apparatus described in a

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TABLE I. Analytical and Some Physical Data of Antimony(III) and (V) Chlorides–Pyridine and Picoline N-Oxides Complexes

Compound	Colour	M.P. (°C)	%M	%C	%N	%H
SbCl ₃ ·PyO	White	105–110	36.94(37.67) ^a	19.85(18.60)	4.80(4.30)	1.71(1.50)
SbCl ₃ ·(4-PicO) ₂	Pale Yellow	135	27.55(27.28)	32.19(32.20)	6.31(6.20)	3.21(3.10)
SbCl ₃ ·PyO	White	190	-----	15.26(15.20)	3.56(3.50)	1.35(1.20)
SbCl ₃ ·2-PicO	Yellow	110–120	-----	19.00(17.60)	3.70(3.40)	2.01(1.70)
SbCl ₃ ·3-PicO	Yellow	155–160	-----	18.30(17.60)	3.50(3.40)	1.88(1.70)
SbCl ₃ ·4-PicO	White	235	-----	17.45(17.60)	3.36(3.40)	1.78(1.70)

^a The theoretical percentage is given in brackets.

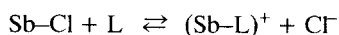
previous paper⁸. The dipole moments were determined in benzene, at 25°C, on the basis of the method described by Guggenheim⁹, using dielectrometric titrations and refraction index measurements^{10,11}. The IR spectra were recorded in potassium bromide pellets or Nujol mulls in polyethylene windows using a Beckman IR-20A spectrophotometer. As far as possible, a dry box was used for manipulations.

Results and Discussion

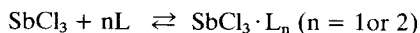
SbCl₃

The progress of the reaction between pyridine N-oxide and antimony(III) chloride in 1,2-dichloroethane was studied titrimetrically by spectrophotometry and conductometry.

The conductometric curves (Fig. 1) show increases of specific conductivity until it reaches a maximum for the MR 1:2, where it begins to decrease. Until it reaches MR 1:1 curve variation is practically linear. Similar behaviour was observed when confronting SbCl₃ with DMSO, TBP, and HMPA¹². As suggested in these cases, this conductivity increase could be due to slight ionization processes of the type:



superimposed on the formation equilibrium of the adducts,



The spectrophotometric measurements were centred in the bands of the ligands. According to theoretic studies¹³, the associated transition with the bands imply a charge transfer from the N–O oxygen to the ring. This phenomenon should be affected when the oxygen atom involves part of its free electron pairs in a donor–acceptor process.

In the spectrophotometric titrations, a blue shift of the $\pi \rightarrow \pi^*$ band was observed when the MR was 1:1 or 1:2. In the first case, the displacements occurred between 3 and 6.5 nm, being greater when L = 4-PicO and lesser when L = 2-PicO. The hypsochromic shift was less significant for the MR 1:2. Similar behaviour

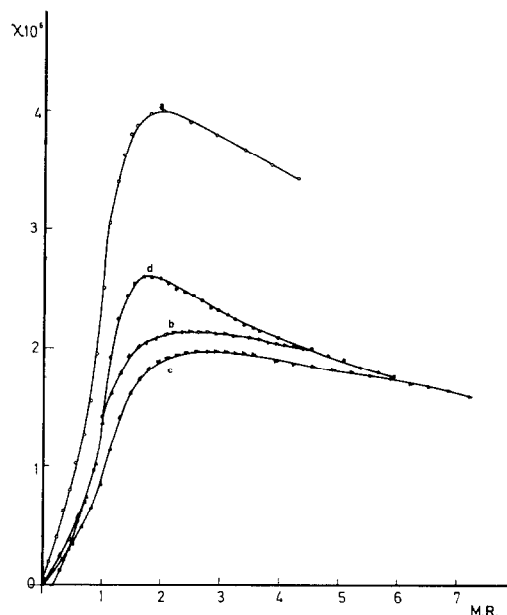


Figure 1. Conductometric titrations in 1,2-dichloroethane of SbCl₃ with: (a) PyO, (b) 2-PicO, (c) 3-PicO, (d) 4-PicO.

was observed in complexes of titanyl, zirconyl and uranyl perchlorates with pyridine N-oxides^{14,15}.

The dielectrometric titrations together with refractometric data allowed the calculations of Guggenheim parameters α and ν , and the dipole moments of the adducts 1:1 and 1:2 (Table II). The results are compatible with bipyramidal–trigonal structures for the SbCl₃·L complexes, with a lone pair of the central atom in a coordination position, a situation similar to the one found for the SbCl₃·C₆H₅NH₂ adduct in solid state¹⁶. The values of the moments of the SbCl₃·L₂ compounds proved too low for an octahedral structure with an active pair and the donor molecules in *cis* position – a coordination found by Hulme *et al.*¹⁷ in solid phase for the complex SbCl₃·(C₆H₅NH₂)₂. This discrepancy is justifiable if an equilibrium between *cis* and *trans* forms exists in solution.

Only two of the adducts isolated have shown a defined composition (Table I). The adduct SbCl₃·

TABLE II. Dipole Moments of Complexes in Benzene at 25°C.

Complex	α	ν	$\mu(\text{D})$	$\mu_{\text{L-A}}(\text{D})$
$\text{SbCl}_3 \cdot \text{PyO}$	39.6053	2.7255	10.5 ^a	-----
$\text{SbCl}_3 \cdot (\text{PyO})_2$	35.8803	2.2206	11.4 ^a	-----
$\text{SbCl}_3 \cdot 2\text{-PicO}$	28.4559	0.3743	9.3	-----
$\text{SbCl}_3 \cdot (2\text{-PicO})_2$	23.2537	0.3599	9.7	-----
$\text{SbCl}_3 \cdot 3\text{-PicO}$	22.1540	0.3990	8.2	-----
$\text{SbCl}_3 \cdot (3\text{-PicO})_2$	18.1886	0.5574	8.5	-----
$\text{SbCl}_3 \cdot 4\text{-PicO}$	31.1642	0.2032	9.8	-----
$\text{SbCl}_3 \cdot (4\text{-PicO})_2$	26.3477	0.4205	10.3	-----
$\text{SbCl}_5 \cdot \text{PyO}$	36.3453	0.7944	11.4 ^a	5.8
$\text{SbCl}_5 \cdot 2\text{-PicO}$	31.3913	0.3366	10.8	5.2
$\text{SbCl}_5 \cdot 3\text{-PicO}$	33.7786	0.4329	11.2	5.4
$\text{SbCl}_5 \cdot 4\text{-PicO}$	45.4977	0.0294	13.1	7.1

^a The error of this values is greater than the others because they have been calculated from very diluted solutions.

TABLE III. More Relevant IR Frequencies (cm^{-1}) of Compounds.

Compound	$\nu_{\text{N-O}}$	$\nu_{\text{Sb-Cl}}$	$\nu_{\text{Sb-O}}$
PyO	1250 vs	-----	-----
2-PicO	1250 vs	-----	-----
3-PicO	1278 vs	-----	-----
4-PicO	1249 vs	-----	-----
$\text{SbCl}_3 \cdot \text{PyO}$	1200 vs	320 s, 300 s	360 m
$\text{SbCl}_3 \cdot (4\text{-PicO})_2$	1200 vs, 1192 vs	320 w, 290 m	375 m
$\text{SbCl}_5 \cdot \text{PyO}$	1192 vs	350 vs, 315 m	400 s
$\text{SbCl}_5 \cdot 2\text{-PicO}$	1195 vs	360 vs, 345 vs, 320 m	410 s
$\text{SbCl}_5 \cdot 3\text{-PicO}$	1242 m	360 vs, 345 vs, 320 m	405 s
$\text{SbCl}_5 \cdot 4\text{-PicO}$	1200 vs	360 s, 345 vs, 330 m	440 s

(4-PicO)₂ exhibited in acetonitrile a molar conductivity (for a solution $10^{-3}M$) of $2.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ showing a non-electrolytic nature¹⁸. The compound $\text{SbCl}_3 \cdot \text{PyO}$ was practically insoluble in this solvent.

Because of complex formation the IR spectra presented (Table III) a shift towards lower frequencies for the $\nu_{\text{N-O}}$ band exhibited by the free ligands. This is indicative of coordination through the N-O oxygen. In the complex $\text{SbCl}_3 \cdot (4\text{-PicO})_2$, a splitting of this band was observed, which could be caused by the coupling of the vibrations of both molecules of ligand in the solid. The $\delta_{\text{N-O}}$ and $\gamma_{\text{C-H}}$ ligand modes undergo modifications of little significance. In Table III, $\nu_{\text{Sb-O}}$ and $\nu_{\text{Sb-Cl}}$ modes are assigned in a very tentative form. The uncertainty comes from the facility with which bands can be mistaken in the complexes of SbCl_3 and AsCl_3 ¹⁹. The antimony-oxygen bands appear in these systems at lower frequencies than in the corresponding adducts of SbCl_5 (*vide infra*) in agreement with the acid forces of the two antimony halides¹⁹.

SbCl_5

The conductometric titrations in 1,2-dichloroethane showed inflexions around the MR 1:1 and conductivity

variations with time in the proximities of this point, suggesting the presence of various superimposed equilibria of mutual influence.

The UV spectra of acceptor-donor mixture in MR 1:1 show blue shifts of $\pi-\pi^*$ bands of the ligands between 9 and 17 nm and also increases in the extinction coefficients. Again the lesser shift corresponds to 2-PicO and the greater to 4-PicO.

The dielectrometric titrations (Fig. 2) together with refractometric data allow the calculation of the dipole moments of the adducts 1:1 (Table II) which do not disagree with those given in the literature²⁰⁻²⁴. These values can be related with the moments of the donor-acceptor bonds in making certain structural considerations. On the basis of a C_{4v} configuration for the adducts in solution (structure confirmed in solid state by the IR spectra, *vide infra*) and supposing an angle $\text{Sb-O-N} = 120^\circ$ (very frequent value in the complexes of pyridine N-oxides of diverse geometry²⁵), the components of the total dipolar moment could be expressed as:

$$\begin{aligned}\mu_x &= \mu_L \cos 30^\circ \\ \mu_y &= 0 \\ \mu_z &= \mu_{\text{Sb-Cl}} + \mu_{\text{L-A}} + \mu_L \cos 60^\circ\end{aligned}\quad (1)$$

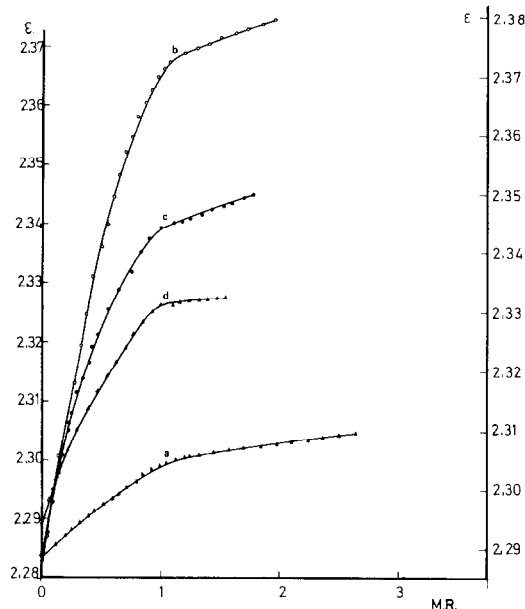


Figure 2. Dielectrometric titrations in benzene of SbCl_5 with: (a) PyO, (b) 2-PicO, (c) 3-PicO, (d) 4-PicO. The right ordinate axis is for curve b. The concentration of initial acceptor solutions is between $2\text{--}8 \times 10^{-3} \text{ M}$.

where xy is the plane containing the four equatorial chlorines, μ_L the dipole moment of the pyridine N-oxides, and $\mu_{\text{Sb-Cl}}$ and $\mu_{\text{L-A}}$ the moments of Sb-Cl and donor-acceptor bonds, respectively. Smyth²⁶ proposes a value of 2.6 D for $\mu_{\text{Sb-Cl}}$. Supposing that the partial cession of the base pair increases the bond polarity, a value of 3 D could be considered acceptable for this moment. The values taken for μ_L were $\mu_{\text{PyO}} = 4.2 \text{ D}^{27}$, $\mu_{2\text{-PicO}} = 3.9 \text{ D}^{25*}$, $\mu_{3\text{-PicO}} = 4.3 \text{ D}^{27}$ and $\mu_{4\text{-PicO}} = 4.5 \text{ D}^{27}$. Substituting these values in (1), the moments of donor-acceptor bonds of Table II are obtained. Although the quantitative aspect of these values could be affected by the assumptions made above, since the error would probably affect all the complexes in the same way, the qualitative sequence of $\mu_{\text{L-A}}$ should prove to be fundamentally correct. On the other hand these values proved to agree with those stated in the literature for the strong acceptors and donors²³, but higher than those found when SbCl_5 interacts with weaker donors²⁴. This indicates an important charge transfer from the donor to the acceptor and a greater basicity for 4-PicO as was expected according to the values of $\sigma_{\text{PyNO}}^{1,28}$ for the different oxides.

The isolated complexes have the general stoichiometry $\text{SbCl}_5 \cdot \text{L}$ (Table I). The adducts of 2-PicO and 3-PicO retain an excess of ligand, mainly the first one. Because of the crystallization difficulty shown by these

complexes, such excess could not be eliminated. Adducts are non-conducting in acetonitrile¹⁸, with values of molar conductivity (for solutions 10^{-3} M) between $1\text{--}2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

The IR spectra show shifts of the $\nu_{\text{N-O}}$ frequency towards lower wavenumbers (Table III). The $\delta_{\text{N-O}}$ bands is displaced in the same way. The $\nu_{\text{Sb-Cl}}$ was assigned taking into account the position of this band in SbCl_5 ²⁹ and the fact that an increase of coordination in the Sb(V) environment should lower the frequency of vibration of these bonds³⁰. The bands found are in agreement with C_{4v} structures for the complexes, so that such a situation could imply the existence of three $\nu_{\text{Sb-Cl}}$ and one $\nu_{\text{Sb-O}}$ IR active bands situated in the analyzed zone³¹. Furthermore, the values of Table III match qualitatively with the position of the bands shown by SbCl_5Br^- ion³¹.

The assignment of the band $\nu_{\text{Sb-O}}$ in $\text{SbCl}_5 \cdot \text{PyO}$ implied choosing between two absorptions recorded at 400 and 440 cm^{-1} , the latter being next to the frequencies $\nu_{\text{Sb-O}}$ reported in literature^{6,32}. Nevertheless, this band also appears in $\text{SbCl}_3 \cdot \text{PyO}$, so that it is probably originated from the ligand. This was considered by Brown *et al.*³ and Kawasaki *et al.*³³ in the complexes they prepared with pyridine N-oxide. Therefore it appears more suitable to consider the band situated at 400 cm^{-1} as $\nu_{\text{Sb-O}}$.

For the rest of SbCl_5 complexes, $\nu_{\text{Sb-O}}$ has been assigned taking the adduct of PyO as reference. The sequence obtained agrees qualitatively with that expected from the different pyridine and picoline N-oxide basicities. Nevertheless the plot of $\nu_{\text{Sb-O}}$ versus σ_{PyNO} shows a poor linear relation between both quantities, possibly due to the bands $\nu_{\text{Sb-O}}$ not being 'pure' because they contain a mixture of ligand bands³⁴.

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